

We claim:

1. A process for preparing optionally alkyl-substituted 1,4-butanediol by two-stage catalytic hydrogenation in the gas phase of C₄-dicarboxylic acids and/or of derivatives thereof having the following steps:

a) introducing a gas stream of a C₄-dicarboxylic acid or of a derivative thereof at from 200 to 300°C and from 2 to 60 bar into a first reactor and catalytically hydrogenating it to a product which contains mainly optionally alkyl-substituted γ -butyrolactone;

b) converting the product stream into the liquid phase;

c) introducing the product stream obtained in this way into a second reactor at a temperature of from 100°C to 240°C and a pressure of from 20 to 250 bar and catalytically hydrogenating it in the liquid phase to optionally alkyl-substituted 1,4-butanediol;

d) removing the desired product from by-products and any unconverted reactant;

e) optionally recycling unconverted intermediates into one or both hydrogenation stages,

said hydrogenation stages both using a catalyst which comprises $\leq 95\%$ by weight, preferably from 5 to 95% by weight, in particular from 10 to 80% by weight, of CuO, and $\geq 5\%$ by weight, preferably from 5 to 95% by weight, in particular from 20 to 90% by weight, of a support, said second reactor having a higher pressure than said first reactor, and the product mixture removed from said first reactor being introduced without further purification into said second reactor.

2. A process as claimed in claim 1, wherein the entrance temperature into the first reactor is from 235 to 270°C and the entrance temperature into the second reactor is from 120°C to 200°C, in particular from 140 to 180°C.

3. A process as claimed in claim 1 or 2, wherein the hot spot temperature in the first reactor is from 210 to 310°C, preferably from 245 to 280°C, and the process is carried out in such a manner that the hot spot temperature is above the entrance temperature and the exit temperature of the reaction gases, and is from 5 to 30°C, in particular from 5 to 15°C, more preferably from 5 to 10°C, above the entrance temperature.
4. A process as claimed in any of claims 1 to 3, wherein the pressure in the first hydrogenation stage is from 2 to 20 bar, preferably from 5 to 15 bar, and the pressure in the second hydrogenation stage is from 60 to 200 bar, preferably from 80 to 160 bar.
5. A process as claimed in any of claims 1 to 4, wherein the catalyst hourly space velocity of the first hydrogenation stage is in the range from 0.02 to 1, in particular from 0.05 to 0.5, kg of reactant/l catalyst · hour, and the catalyst hourly space velocity of the second hydrogenation stage is in the range from 0.02 to 1.5, in particular from 0.1 to 1, kg of reactant/l of catalyst · hour.
6. A process as claimed in any of claims 1 to 5, wherein the hydrogen/reactant molar ratio in both reaction stages is > 5, preferably from 20 to 600.
7. A process as claimed in claim 6, wherein the hydrogen/reactant ratio in the first stage hydrogenation is from 20 to 200, preferably from 40 to 150, in particular from 50 to 100.
8. A process as claimed in any of claims 1 to 7, wherein the reactors used in the first and second hydrogenation stages are selected from the group consisting of tubular reactors, shaft reactors, reactors having internal heat removal means, tube bundle reactors and fluidized bed reactors.
9. A process as claimed in claim 8, wherein a tube bundle reactor is used in the first hydrogenation stage.
10. A process as claimed in claim 8 or 9, wherein a loop or shaft reactor is used in the second hydrogenation stage.

11. A process as claimed in any of claims 1 to 10, wherein the hydrogenation in the second stage is carried out as a suspension hydrogenation or fixed-bed hydrogenation, in particular as a fixed-bed hydrogenation.
- 5 12. A process as claimed in any of claims 1 to 11, wherein more than one reactor connected in parallel or in series is used in the first and/or second hydrogenation stage.
- 10 13. A process as claimed in any of claims 1 to 12, wherein the support material of the catalyst is selected from the group of ZnO, Al₂O₃, SiO₂, TiO₂, ZrO₂, CeO₂, MgO, CaO, SrO, carbon of varying origin, BaO and Mn₂O₃ and mixtures thereof, preferably from the group of ZnO/Al₂O₃ mixtures, the delta-, theta-, alpha- and eta-modifications of Al₂O₃ and also mixtures which comprise at least one component each firstly from the group of SiO₂, TiO₂, ZrO₂, and secondly from the group of
15 ZnO, MgO, CaO, SrO and BaO.
14. A process as claimed in any of claims 1 to 13, wherein the support material is selected from ZnO, ZnO/Al₂O₃ mixtures in a weight ratio of from 100:1 to 1:2 and mixtures of SiO₂ with MgO, CaO and/or ZnO in a weight ratio of 200:1 to 1:1.
20
15. A process as claimed in any of claims 1 to 14, wherein the catalyst comprises one or more further metals, preferably Pd, or a compound of one or more further metals, preferably an oxide, from groups 1 to 14 of the Periodic Table.
- 25 16. A process as claimed in any of claims 1 to 15, wherein the catalyst is used in the form of shaped bodies, preferably in the form of extrudates, ribbed extrudates, tablets, rings, spheres or spall.
- 30 17. A process as claimed in any of claims 1 to 16, wherein the BET surface area of the copper catalysts in the oxidic state is from 10 to 1 500 m²/g, preferably from 10 to 300 m²/g, more preferably from 15 to 175 m²/g, in particular from 20 to 150 m²/g.
- 35 18. A process as claimed in any of claims 1 to 17, wherein the copper surface area of the reduced catalyst in the installed state is > 0.2 m²/g, preferably > 1 m²/g, in particular > 2 m²/g.

19. A process as claimed in any of claims 1 to 18, wherein the catalysts used in the first and second reactors are identical or different, preferably different.
20. A process as claimed in any of claims 1 to 19, wherein the shaped bodies of the catalyst used have a pore volume of > 0.01 ml/g for pore diameters of > 50 nm, preferably of > 0.025 ml/g for pore diameters of > 100 nm and in particular of > 0.05 ml/g for pore diameters of > 200 nm.
21. A process as claimed in any of claims 1 to 20, wherein the ratio of micropores having a diameter of > 50 nm to the total pore volume for pores having a diameter of > 4 nm is $> 10\%$, preferably $> 20\%$, in particular $> 30\%$.
22. A process as claimed in any of claims 1 to 21, wherein the reactant used in the reaction is maleic anhydride.
23. A process as claimed in any of claims 1 to 22, wherein maleic anhydride is used which has been prepared by oxidizing benzene, C_4 -olefins or n-butane, and the crude maleic anhydride obtained by oxidation has been extracted from the crude product mixture using a solvent and then stripped from this solvent using hydrogen.
24. A process as claimed in any of claims 1 to 23, wherein the absorbent is selected from the group consisting of tricresyl phosphate, dibutyl maleate, high molecular weight waxes, aromatic hydrocarbons having a molecular weight of from 150 to 400 and a boiling point above 140°C , preferably dibenzene, di- C_1 - C_4 -alkyl esters of aromatic and aliphatic dicarboxylic acids, preferably dimethyl 2,3-naphthalenedicarboxylate and/or dimethyl 1,4-cyclohexanedicarboxylate, methyl esters of long-chain fatty acids having from 14 to 30 carbon atoms, high-boiling ethers, preferably dimethyl ethers of polyethylene glycol, preferably of tetraethylene glycol, and alkyl phthalates and dialkyl phthalates having C_1 - C_{18} -alkyl groups, preferably from the group of dimethyl phthalate, diethyl phthalate, dibutyl phthalate, di-n-propyl and diisopropyl phthalate, undecyl phthalate and diundecyl phthalate.
25. A process as claimed in any of claims 1 to 24, wherein the maleic anhydride is stripped from the absorbent under reduced pressure or pressures which correspond to the hydrogenation pressure or are a maximum of 10% above this pressure.

26. A process as claimed in any of claims 1 to 25, which is carried out batchwise, semicontinuously or continuously, preferably continuously.
- 5 27. A process as claimed in any of claims 1 to 26, wherein hydrogen is removed from the liquid stream of the first hydrogenation before it is introduced into the second hydrogenation.
- 10 28. A process as claimed in any of claims 1 to 27, wherein the water of reaction formed is substantially removed from the condensed product stream before it enters the second hydrogenation reactor.